

Pairing mechanism in Fe pnictide superconductors

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By applying an *exact* unitary transformation to a two-band hamiltonian which also includes the effects due to large pnictogen polarizabilities, we show that an attractive spin-mediated Hubbard term appears in the d_{xz} , d_{yz} nearest-neighbour channel. This pairing mechanism implies a singlet superconducting order parameter in iron pnictides.

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The recent observation of high temperature superconductivity in Fe pnictide compounds [1] has generated a huge interest and a large research effort. As a result four families of compounds have emerged having similar properties and exhibiting superconductivity. Namely, chalcogenides (FeSe and FeTe) and three families of pnictides (represented by LaOFeAs, BaFe₂As₂, and LiFeAs).

Band structure calculations have revealed that (i) electron-phonon coupling alone cannot account for the high values of T_c [2], (ii) nesting between the hole Fermi surfaces at zone center and the electron Fermi surfaces around the zone corner may play a significant role both in magnetism and superconductivity [3]. These results have prompted the idea that the pairing glue is provided by spin fluctuations exchange between electrons in different bands [3, 4]. However, NMR studies measuring the temperature dependence of nuclear spin-lattice relaxation rate ($1/T_1$) suggest that spin fluctuations may not be important in iron-pnictide superconductivity [5]. Thus other pairing mechanisms have to be responsible for the unusually high superconducting critical transition temperature.

In the following we will present the results of an *exact* unitary (canonical) transformation (UT) by which it can be shown rigorously that an attractive spin-mediated Hubbard term appears in the d_{xz} , d_{yz} nearest-neighbour channel. The mechanism is similar to a spin double-exchange type and hence has origins of a kinetic mechanism.

We start with the by now familiar two-band model description of the FeAs superconductors [6]. We take a two-dimensional square lattice with d_{xz} and d_{yz} orbitals per site. For simplicity we label the d_{xz} and d_{yz} orbitals by a and b , respectively. The kinetic energy component can be expressed as:

$$H_{\text{kin}} = -\frac{1}{2} \sum_{\mathbf{ij}, \sigma} \sum_{\alpha, \beta=a, b} t_{\alpha\beta} (\alpha_{\mathbf{i}, \sigma}^\dagger \beta_{\mathbf{j}, \sigma} + \text{h.c.}) . \quad (1)$$

Here, the site indices, \mathbf{i} and \mathbf{j} , run over nearest and next-nearest neighbors. The effective hoppings, $t_{\alpha\beta}$, have contributions from both direct Fe-Fe and Fe-As-Fe processes.

If the simplified description of a Slater-Koster formalism [7] is adopted, then t_{ab} , the matrix element between d_{xz} and d_{yz} orbitals on nearest neighbor sites, is zero because the formalism assumes perfect spherical symmetry. However, in models that use all five Fe $3d$ orbitals, t_{ab} is non-zero [4, 8]. In fact, according to Ref. [8], $t_{ab} = 0.54$ eV is the largest Fe-Fe hopping integral. Consequently, we take the view that the two-band model can be extracted from a more general model by focusing on its relevant 2×2 block. The parameter t_{ab} is crucial because, as will be discussed below, it will be at the basis of the UT (see, Eq. (4)). The other hopping parameters enter into our UT formulation through the bandwidth, ε , which we take as 2 eV [4, 6, 8, 9].

$H_{\text{int}} = \sum_{\mathbf{i}} H_{\mathbf{i}}$ contains only on-site contributions, with

$$H_{\mathbf{i}} = \sum_{\alpha} U_{\alpha} n_{\mathbf{i}, \alpha, \uparrow} n_{\mathbf{i}, \alpha, \downarrow} + (U' - J/2) \sum_{\mathbf{i}} n_{\mathbf{i}, a} n_{\mathbf{i}, b} - 2J \mathbf{S}_{\mathbf{i}, a} \cdot \mathbf{S}_{\mathbf{i}, b} + J' (a_{\mathbf{i}, \uparrow}^\dagger a_{\mathbf{i}, \downarrow}^\dagger b_{\mathbf{i}, \downarrow} b_{\mathbf{i}, \uparrow} + \text{h.c.}) . \quad (2)$$

As in Eq. (1), $\alpha = a, b$ labels d_{xz}, d_{yz} orbitals. $\mathbf{S}_{\mathbf{i}, \alpha}$ ($n_{\mathbf{i}, \alpha, \sigma}$) is the spin (density) in orbital α at site \mathbf{i} . Following Refs. [6], we used $U' = U - 2J$ and the pair hopping term strength $J' = J$, where J is the Hund coupling.

The onsite Hubbard terms are obviously equal, $U_a = U_b = U$, with U chosen between 3.0 - 4.5 eV. Although in the literature there is no agreement on whether the iron pnictides should be considered as strongly correlated or, at most, moderately correlated materials, there is more consensus regarding the strength of U to be 4 eV [10], 3.5 eV [11] or even smaller $U \geq 2$ eV [12]. In our UT approach described below, U' and J give rise to no new physics, although they do render the transformation algebra very complicated. Thus, only at the end their effect on the final result will be briefly discussed.

The third and last contribution that we include in our starting hamiltonian is the polarizability effect. As pointed out already in Ref. [13] the polarizability effects in iron pnictides are much larger than in copper-base high T_c 's. In fact, it is known [14] that the ions As^{3-} and Se^{2-} have huge polarizabilities, mainly due to the fact that their volume is very large. Hence, whenever an iron site is charged due to electrons hopping to or from it,

the surrounding As or Se atoms will easily get polarized, an effect we need to capture.

The effect of As (or Se) polarizability on iron sites can be described by writing [15] the hamiltonian term first introduced in Ref. [16] per iron site as $g n (p^\dagger s + s^\dagger p)$. Here the possible excitations of an As electron from $4p$ to unoccupied $5s$ are taken into account with an effective coupling, denoted by g , due to a charge on Fe. The $n = n_\uparrow + n_\downarrow$ notation ($n = n_a$ or n_b) is identical to the one used in Eq. (2) and describes Fe $3d$ electrons.

The angle dependence between the As p and s orbitals was extensively studied already [17], hence we only consider a simplified version of the hamiltonian taking into account only the mean total polarizability per bond [15, 16] by a hamiltonian term of the form: $H_{\text{pol}} = P \sum_{\langle i,j \rangle} (n_i - n_j)$, where $P = g \langle p^\dagger s + s^\dagger p \rangle$ will be the measure of As average polarizability, with P estimated to be around 2eV [17]. In this way our starting hamiltonian is $H_{\text{kin}} + H_{\text{int}} + H_{\text{pol}}$.

One of the most common tools used in theoretical physics is perturbation theory. Here, we present a perturbation theory which we solve *exactly* using a UT. There are two reasons for using UT [18]: *i*) the belief that the transformed Hamiltonian is “simpler” in the sense that it is “more diagonal” and *ii*) the desire to gain a deeper physical insight into the problem, given that the transformed Hamiltonian may reveal the appropriate independent subsystems. Our scope is to pursue the latter.

For the UT to work, we separate out from H_{kin} the diagonal hopping term, $H_{ab} = t_{ab} \sum_{\langle i,j \rangle, \sigma} (a_{i,\sigma}^\dagger b_{j,\sigma} + \text{h.c.})$. Hence we can write $H_{\text{kin}} = H_0 + H_{ab}$, where H_0 contains the remaining terms other than t_{ab} . To be more transparent, we re-write our starting hamiltonian as $H + H_{ab}$, where $H \equiv H_0 + H_{\text{int}} + H_{\text{pol}}$. H will be the zeroth-order hamiltonian and t_{ab} the perturbation.

It is known [19, 20] that in fourth order perturbation an attractive Hubbard type carrier-carrier interaction appears, parallel to spin-carrier, spin-spin, carrier-carrier-spin, etc. terms [21, 22]. All these terms are spin mediated, of superexchange type [19, 20], and hence with physical origins of a kinetic mechanism [23]. The attractive carrier-carrier terms that we are interested in appear either onsite or between nearest-neighbor sites [19, 20]. However, performing a perturbation up to fourth order is not enough to draw a final conclusion, as was pointed out in Ref. [20]. Depending upon the value of input parameters, the second, sixth, etc., order terms may well give repulsive interactions, while the fourth, eighth, etc., attractive ones [22]. Thus, higher contributions need to be calculated in order to verify the convergence.

Hence, initially we check for the convergence of higher order terms for the particular case of Fe pnictides. In a standard UT [18, 19, 20, 21, 22] the transformed Hamiltonian $e^{\mathcal{S}}(H + H_{ab})e^{-\mathcal{S}}$ is identical to $H + \sum_{n=1}^{\infty} [1/n! -$

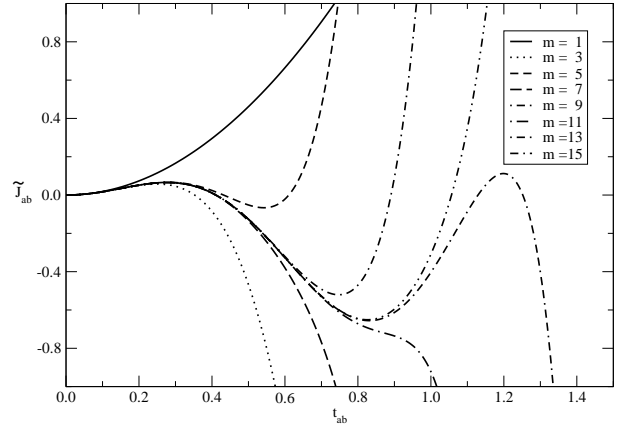


FIG. 1: The calculated superexchange interaction \tilde{J}_{ab} in different orders n , as defined in Eq. (3). We show the total contributions for each order, i.e., $\sum_{n=1}^m [1/n! - 1/(n+1)!] \tilde{H}_n$, see also Ref. [24]. For input parameters we used $\varepsilon = 2\text{eV}$, $P = 2\text{eV}$ and $U = 4.5\text{eV}$.

$1/(n+1)! \tilde{H}_n$ (henceforth, \sim denotes a UT result), where

$$\tilde{H}_n = \overbrace{[\mathcal{S}, [\mathcal{S}, [\mathcal{S}, \dots [\mathcal{S}, H_{ab}] \dots]]]}^{n \text{ times}} \quad (3)$$

for an \mathcal{S} which satisfies $H_{ab} + [\mathcal{S}, H] = 0$. Using the notations: $\mathcal{C}_1 = 1/(\varepsilon + P)$, $\mathcal{C}_2 = 1/(\varepsilon + P + U_b) - \mathcal{C}_1$, $\mathcal{C}_3 = 1/(\varepsilon + P - U_a) - \mathcal{C}_1$, and $\mathcal{C}_4 = 1/(\varepsilon + P + U_b - U_a) - 1/(\varepsilon + P + U_b) - 1/(\varepsilon + P - U_a) + \mathcal{C}_1$, the unitary operator \mathcal{S} is:

$$\mathcal{S} = -t_{ab} \sum_{\langle i,j \rangle, \sigma} (\mathcal{C}_1 + \mathcal{C}_2 n_{j,-\sigma}^b + \mathcal{C}_3 n_{i,-\sigma}^a + \mathcal{C}_4 n_{i,-\sigma}^a n_{j,-\sigma}^b) (a_{i,\sigma}^\dagger b_{j,\sigma} - \text{h.c.}) \quad (4)$$

The first order UT (i.e., second order perturbation theory [25]) can be readily performed. This result is well known [20, 22], and consequently not pursued further. In the second and all other ‘even’ order transformations, H_{ab} is recovered structurally with the addition of all possible correlated hopping terms [18, 20]: $H_{n=\text{even}} = \sum_{\langle i,j \rangle, \sigma} [\tilde{t}_{ab} + \tilde{t}_{ab}^a n_{i,-\sigma}^a + \tilde{t}_{ab}^b n_{j,-\sigma}^b + \tilde{t}_{ab}^{ab} n_{i,-\sigma}^a n_{j,-\sigma}^b] (a_{i,\sigma}^\dagger b_{j,\sigma} + \text{h.c.})$.

Consequently, the weight of the original t_{ab} is redistributed in every order of the transformation among \tilde{t}_{ab} , \tilde{t}_{ab}^a , \tilde{t}_{ab}^b and \tilde{t}_{ab}^{ab} . Because of the smallness of U in Fe pnictides, as the UT is performed to higher orders weight is shifted in and out of the correlated hopping terms generating an oscillatory behavior. These oscillations are well-known [18, 20, 22] in standard perturbation theory. As an example, the Heisenberg superexchange term \tilde{J}_{ab} is shown in Fig. 1 for high orders. Hence, the problem with applying standard UT is that unless U is very large, the perturbation series will not converge.

To overcome this problem, a completely new approach is needed to handle Fe pnictide case, i.e., to perform an

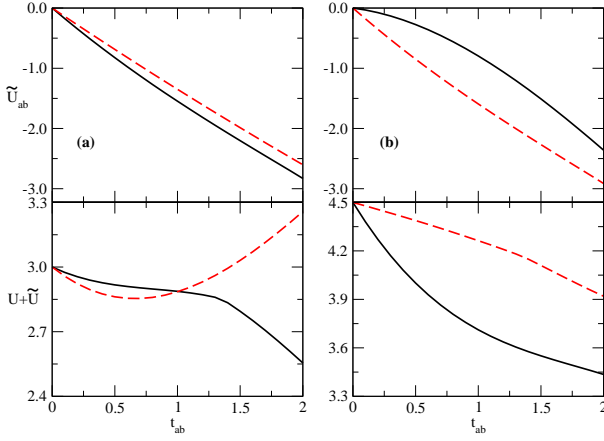


FIG. 2: (Color online) The calculated nearest neighbor, \tilde{U}_{ab} (top), and the total onsite, U (initial value) + \tilde{U} (calculated value) (bottom), Hubbard coefficients as a function of t_{ab} . Input parameters are $\varepsilon = 2\text{eV}$, $U = 3\text{eV}$ [part (a)] and $U = 4.5\text{eV}$ [part (b)]. Continuous (black) curves are $P = 1.5\text{eV}$, while long-dashed (red) curves are for $P = 3\text{eV}$.

exact UT. We have chosen to perform such a transformation by eliminating three consecutive even order terms simultaneously (the $n = 0$, $n = 2$ and $n = 4$ order terms) from Eq. (3) via a new unitary operator \mathcal{S} such that

$$H_{ab} + [\mathcal{S}, H] + \frac{1}{2!}[\mathcal{S}, [\mathcal{S}, H_{ab}]] = 0. \quad (5)$$

This guarantees that the transformation cannot be continued to higher orders, since all $a \leftrightarrow b$ hopping processes are eliminated, as \tilde{t}_{ab} and the correlated hopping terms, \tilde{t}_{ab}^a , \tilde{t}_{ab}^b , \tilde{t}_{ab}^{ab} are strictly zero. Accordingly, the transformed hamiltonian

$$e^{\mathcal{S}}(H + H_{ab})e^{-\mathcal{S}} = H + [\mathcal{S}, H_{ab}] + \frac{1}{2!}[\mathcal{S}, [\mathcal{S}, H]], \quad (6)$$

is exact in a strict mathematical sense [18]. Eq. (6) is merely a self-consistent mixing [18] of the $n=1$ and $n=3$ order standard UT, i.e., of a standard 2nd and 4th order perturbation theory [25]. This guarantees that we can capture the whole spectrum of the carrier-carrier interaction terms [19, 20].

The solution of Eq. (5) has the same algebraic form as Eq. (4) with new coefficients \mathcal{C}_1 , \mathcal{C}_2 , \mathcal{C}_3 and \mathcal{C}_4 as unknown parameters. These are determined from Eq. (5), which gives the following systems of equations:

$t_{ab} = t_{ab}[\cos(2t_{ab}\mathcal{C}_1) + (\varepsilon + P)\mathcal{C}_1 \sin(2t_{ab}\mathcal{C}_1)/(2t_{ab}\mathcal{C}_1)]$
 $\tilde{t}_{ab}^a = 8t_{ab}^3\mu[(\varepsilon + P)(\mu^2 - \nu^2) - U_a\mu^2 - U_b\nu^2]\phi(2\tau) + 8t_{ab}^3\mu(\mu - \nu)\psi(2\tau) + 4t_{ab}^3\mu\nu^2(\varepsilon + P)\phi(\tau) + 2t_{ab}^3\nu(\mu + \nu)\psi(\tau) - t_{ab}\cos(2t_{ab}\mathcal{C}_1) - (1/2)(\varepsilon + P)\sin(2t_{ab}\mathcal{C}_1)$, where $\mu = \mathcal{C}_1 + \mathcal{C}_2$, $\nu = \mathcal{C}_1 + \mathcal{C}_3$, $\tau = t_{ab}[2(\mu^2 + \nu^2)]^{1/2}$ and the notations $\phi(x) = \sin(x)/x^3$, $\psi(x) = \cos(x)/x^3$ were used. For \tilde{t}_{ab}^b we have to exchange U_a with U_b . Finally, the last of the correlated hopping terms is:

$$\tilde{t}_{ab}^{ab} = -8t_{ab}^3(\mu - \nu)[(\varepsilon + P)(\mu^2 - \nu^2) - U_a\mu^2 - U_b\nu^2]\phi(2\tau) - 8t_{ab}^3(\mu - \nu)^2\psi(2\tau) - 2t_{ab}^3\mu\nu(\mu + \nu)[(\varepsilon + P) -$$

$U_a + U_b]\phi(\tau) - 2t_{ab}^3(\mu + \nu)^2\psi(\tau) + t_{ab}(\mathcal{C}_1^2 + \rho^2)\cos(2t_{ab}\rho) + \frac{1}{2}(\varepsilon + P)(1 + \mathcal{C}_1^3/\rho^3)\sin(2t_{ab}\rho) + t_{ab}(1 - \mathcal{C}_1^2/\rho^2)[1 + (\varepsilon + P)\mathcal{C}_1]$, where $\rho = \mathcal{C}_1 + \mathcal{C}_2 + \mathcal{C}_3 + \mathcal{C}_4$ and note that these equations can also be used if $U_a \neq U_b$.

We calculated numerically the parameters \mathcal{C}_1 , \mathcal{C}_2 , \mathcal{C}_3 and \mathcal{C}_4 from the above system of equations by setting \tilde{t}_{ab} , \tilde{t}_{ab}^a , \tilde{t}_{ab}^b and \tilde{t}_{ab}^{ab} to zero. The new UT, as any standard perturbation theory, gives several spin-spin, carrier-carrier, spin-carrier onsite, nearest neighbor, next-nearest neighbor, etc. terms. From all these we only calculated explicitly the onsite, $\tilde{U} \sum_{\mathbf{i}} n_{\mathbf{i},\alpha,\uparrow} n_{\mathbf{i},\alpha,\downarrow}$ ($\alpha = a, b$) and nearest neighbor $\tilde{U}_{ab} \sum_{\langle \mathbf{i}, \mathbf{j} \rangle} n_{\mathbf{i},a,\uparrow} n_{\mathbf{j},b,\downarrow}$ Hubbard interactions. The results are plotted in Fig. 2, as a function of t_{ab} , and in Fig. 3 as a function of the polarizability, P .

As can be seen in Fig. 2, a nearest-neighbor inter-orbital attractive Hubbard interaction \tilde{U}_{ab} appears due to a spin-mediated superexchange type mechanism [19, 20]. Being of kinetic origin, the spins are not excited [23], only virtual excitations of onsite singlets occur. The situation is similar to the phonon-mediated attraction: at temperatures well below the Debye scale real phonons are never excited, yet they provide an attraction mechanism between electrons.

The values of \tilde{U}_{ab} in Fig. 2 can be well approximated for small t_{ab} with a line: $\tilde{U}_{ab} \approx -\text{const } t_{ab}$, with the constant being $4\xi(\zeta_+ - \zeta_-) \{ \sin(2[2\xi^2(\zeta_+^2 + \zeta_-^2)]^{1/2}) / (2[2\xi^2(\zeta_+^2 + \zeta_-^2)]^{1/2}) + [\cos(2[2\xi^2(\zeta_+^2 + \zeta_-^2)]^{1/2}) - 1] / (2[2\xi^2(\zeta_+^2 + \zeta_-^2)]^{1/2}) \}$, where $\zeta_{\pm} = 1/[\varepsilon + P \pm U]$, $\xi = \eta/[(\varepsilon + P)^2 - U^2]/[(\varepsilon + P)^2 + U^2]^{1/2}$ and the numerical coefficient η is 0.392 for $\varepsilon + P < U$, or 1.178 otherwise.

The new hamiltonian term, H_{Pol} , which gives a measure of the polarizability is not crucial in obtaining this attractive interaction. Any finite value of bandwidth alone suffices for attraction. In fact, the UT expressions depend only on the sum $\varepsilon + P$, and not separately on either. Thus, polarizability effectively acts as a *bandwidth*. So, Fig. 3 covers a wider range for P to allow for cases with different bandwidth and P values. From Fig. 3, upper panel we observe that the attractive \tilde{U}_{ab} is enhanced rather strongly by P for $\varepsilon + P \gtrsim U$. The strongest attraction occurs around the values of P satisfying $\varepsilon + P \approx U$. Note that, this regime is not accessible by standard perturbation theory, but it works well in an exact UT approach.

An additional effect due to H_{Pol} is the modified screening of the on-site Coulomb repulsion U in the presence of P . In the lower panel of Fig. 3 the net repulsion, $U + \tilde{U}$, is seen to deviate significantly from a roughly constant value ($\leq 3\text{ eV}$ for $U = 3\text{ eV}$, $\approx 4\text{ eV}$ for $U = 4.5\text{ eV}$) only in an interval given by $|\varepsilon + P - U| \leq 0.5\text{ eV} = t_{ab}$. Normally, ligand polarizabilities are expected to increase the screening (smaller net U values), however, when the double exchange is the strongest, it restricts the hopping and as such screening is reduced, similarly to, e.g., manganites [14]. U' and J from Eq. (2), have

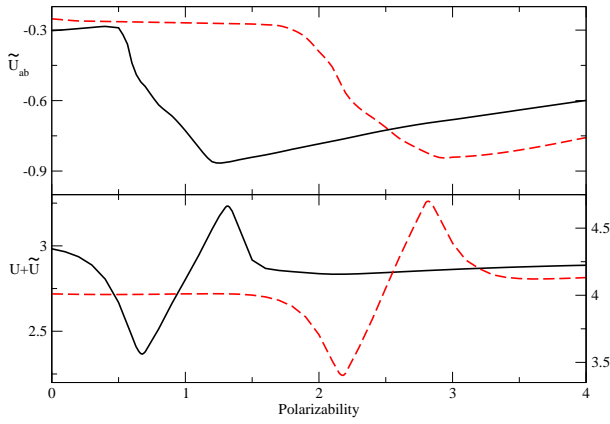


FIG. 3: (Color online) The same Hubbard coefficients as in Fig. 2 as a function of the polarizability, P , for $\varepsilon = 2\text{eV}$ and $t_{ab} = 0.5\text{eV}$. $U = 3\text{eV}$, continuous (black) curves and 4.5eV long dashed (red) curves, respectively. For the lower curves, the left (right) axis is for $U = 3\text{eV}$ (4.5eV).

been neglected up to now. However, their effects in our UT can be accounted for by substituting everywhere U with $U + J(1 - U'/U)/2$. Using the known U' and J values [4, 6, 8, 9, 10, 11, 12] this only causes a less than 5% change in U and hence their effect is minor.

In conclusion we have shown that the Fe pnictide family of alloys exhibit a rather strong pairing interaction, due to a spin-mediated, superexchange type mechanism. There is a quite strong enhancement of the attraction due to the polarizability. However we do not observe polaron and bipolaron formation as in Ref. [17], probably because we are using realistic onsite Hubbard values, instead of $U > 8\text{ eV}$ as used in Ref. [17]. Our pairing mechanism will give rise to a singlet superconducting order parameter. However, in a two-band system the self-consistent solution of the gap equations always has a symmetric (recently denoted as s_{++}) and asymmetric (s_{+-}) solution [26]. In the parameter regime of superconducting Cr alloys, at different concentration of electrons and holes, the asymmetric solution wins [27]. In closing we remark that non-phononic mechanisms support [28] negative isotope effect [29]. The standard isotope effect measured [30] for both superconductivity and itinerant antiferromagnetism in Fe pnictides would require phonon input, which may contradict an electronic mechanism. However, this may not necessarily be the case, as phonons can act as random impurity potentials in certain cases for systems exhibiting electron and hole Fermi surfaces [31]. The pair-breaking effect originating from this also explains why Cr has an isotope effect in T_N . This actually can be very large; the phonons can decrease T_N by as much as 70% from its value in their absence [32]. Another interesting consequence of the pair-breaking by virtual or thermal phonons [32] is that the ratio $2\Delta/k_B T_c$ can be much larger than the BCS value of 3.53.

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- [1] Y. Kamihara, *et al.*, J. Am. Chem. Soc. **130**, 3296 (2008).
 - [2] L. Boeri, *et al.*, Phys. Rev. Lett. **101**, 026403 (2008).
 - [3] I. I. Mazin, *et al.*, Phys. Rev. Lett. **101**, 057003 (2008); A. V. Chubukov, *et al.*, Phys. Rev. **B78**, 134512 (2008).
 - [4] K. Kuroki, *et al.*, Phys. Rev. Lett. **101**, 087004 (2008).
 - [5] N. Terasaki, *et al.*, J. Phys. Soc. Jpn. **78**, 013701 (2009); K. Ishida, *et al.*, J. Phys. Soc. Jpn. **78**, 062001 (2009); Y. Nakai, *et al.*, Phys. Rev. **B79**, 212506 (2009).
 - [6] S. Raghu, *et al.*, Phys. Rev. **B77**, 220503(R) (2008); M. Daghofer, *et al.*, Phys. Rev. Lett. **101**, 237004 (2008); A. Moreo, *et al.*, Phys. Rev. **B79**, 134502 (2009).
 - [7] J.C. Slater and G.F. Koster, Phys. Rev. **94**, 1498 (1954).
 - [8] E. Manousakis, *et al.*, Phys. Rev. **B78**, 205112 (2008).
 - [9] C. Cao, *et al.*, Phys. Rev. **B77**, 220506(R) (2008); K. Nakamura, *et al.*, J. Phys. Soc. Jpn. **77**, 093711 (2008).
 - [10] K. Haule, *et al.*, Phys. Rev. Lett. **100**, 226402 (2008).
 - [11] V.I. Anisimov, *et al.*, Physica **C469**, 442 (2009).
 - [12] W.L. Yang *et al.*, Phys. Rev. **B 80**, 014508 (2009).
 - [13] H. Takahashi, *et al.* Nature **453**, 376 (2008).
 - [14] P. Fulde, *Electron Correlations in Molecules and Solids*, Springer-Verlag, 1991.
 - [15] M. B. J. Meinders, *et al.*, Phys. Rev. **B52**, 2484 (1995).
 - [16] D. K. G. de Boer, *et al.*, Phys. Rev. **B29**, 4401 (1984).
 - [17] G. A. Sawatzky, *et al.*, Europhys. Lett. **86**, 17006 (2009); M. Berciu, *et al.*, Phys. Rev. **B79**, 214507 (2009).
 - [18] M. Wagner, *Unitary Transformations in Solid State Physics*, North-Holland, 1986.
 - [19] V. J. Emery, Phys. Rev. Lett. **58**, 2794 (1987); V. J. Emery and G. Reiter, Phys. Rev. **B38**, 4547 (1988).
 - [20] J. Zaanen and A. M. Oleś, Phys. Rev. **B 37**, 9423 (1988).
 - [21] A. H. MacDonald, *et al.*, Phys. Rev. **B37**, 9753 (1988); E. Kolley and W. Kolley, Phys. Stat. Sol. **157**, 399 (1990); E. Kolley, *et al.*, J. Phys.: Condens. Matter **4**, 3517 (1992); H. Eskes and J. H. Jefferson, Phys. Rev. **B48**, 9788 (1993).
 - [22] M. Gulacsi and R. Chan, Jour. Supercond. **14**, 651 (2001); E. Muller-Hartmann and A. Reischl, Eur. Phys. J. **B28**, 173 (2002); R. Chan and M. Gulacsi, Phil. Mag. **84**, 1265 (2004).
 - [23] P. W. Anderson, Phys. Rev. **115**, 2 (1959).
 - [24] As the number of terms ($2^{1+n+(n-3)/2} 5^{(n-1)/2}$, $n \geq 3$) which contribute to \tilde{J}_{ab} in each individual odd order can reach tens of billions, we used a purpose built algebraic manipulation program to calculate higher orders.
 - [25] The n th order UT transformation of the Eq. (3) type corresponds to an $(n+1)$ th order standard perturbation theory [18].
 - [26] A. I. Rusianov, *et al.*, Sov. Phys. - JETP **38**, 991 (1974).
 - [27] M. Gulacsi and Zs. Gulacsi, Phys. Rev. **B33**, 6147 (1986).
 - [28] D.R. Penn, *et al.*, Phys. Rev. **B47**, 5528 (1993).
 - [29] P. M. Shirage, *et al.*, arXiv:0903.3515 (2009).
 - [30] R. H. Liu, *et al.*, Nature **459**, 64 (2009).
 - [31] A. S. Barker, Jr., *et al.*, Phys. Rev. Lett. **20**, 384 (1968).
 - [32] E. W. Fenton and C. R. Leavens, J. Phys. F: Metal Phys. **10**, 1853 (1980).